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MITIGATING INORGANIC SCALING USING SYNTHETIC ZEOLITE

By

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Dissertation submitted in partial fulfilment of
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CERTIFICATION OF APPROVAL

Mitigating Inorganic Scaling Using Synthetic Zeolite

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A Project Dissertation submitted to the
Chemical Engineering Programme
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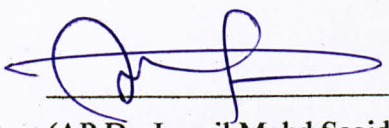
Approved By,



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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified persons or persons.

NUR ASYRAF BT MD AKHIR

ABSTRACT

Inorganic scaling is a predominant formation-damage mechanism in most producing and injection wells worldwide. It occurs in the well tubing and near well bore formations of the production and injection wells. Carbonate and sulfate are two main types of scales commonly found in the oil fields. The deposition of scale on surfaces and production equipment is a major production problem. Scale built-up decreases permeability of the formation, reduces well productivity and shortens the lifetime of production equipment. In this project Zeolite Socony Mobil-5 (ZSM-5) has been used to mitigate the inorganic scaling, as it has high selectivity and high ion exchange capacity. The objectives of this project are to analyze the potential of synthetic zeolite in mitigating inorganic scaling and to examine the changing in permeability of the rocks subjected to the fluid treated with synthetic zeolite. For the scope of study, the literature review on inorganic scaling, synthetic zeolite and permeability of the rock have been done. There are two experiments have been conducted during this project, which are Zeolite Ion Exchange Experiment and Permeability Test. Then, the project is continued with analyzing the sample solution taken from Zeolite Ion Exchange Experiment with X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF). From here, the mineral composition and chemical elements of ZSM-5 can be analyzed. Based on the results obtained from XRF, ZSM-5 has shown its capability in absorbing barium and sodium ions. Meanwhile for the permeability test, there is reduction in permeability of the core samples based on the sample solutions used. These sample solutions that are treated with synthetic zeolite have lower permeability reduction compared to untreated sample solutions. In this study, it is found that synthetic zeolite exhibits potential in mitigating inorganic scaling.

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ABBREVIATIONS & NOMENCLATURES

LIST OF ABBREVIATIONS

BTEX	–	Benzene, Toluene, Ethylbenzene, and Xylenes
HSE	–	Health, Safety and Environment
PRBs	–	Permeable Reactive Barriers
PWRI	–	Produced Water Re-Injection
SEM	–	Scanning Electron Microscope
XRD	–	X-Ray Diffraction
XRF	–	X-Ray Fluorescence
ZSM-5	–	Zeolite Socony Mobil-5

LIST OF NOMENCLATURES

A	–	Cross sectional area of flow in cm^2
Å	–	Ångstrom
Ag^+	–	Silver Ion
Al^{3+}	–	Aluminum Ion
Al_2O_3	–	Aluminum Oxide
Al-Si	–	Alumino-silicates Ion
Ba^{+2}	–	Barium Ion
$BaSO_4$	–	Barium Sulfate
Ca^{+2}	–	Calcium Ion
CaO	–	Calcium Oxide
$CaSO_4$	–	Calcium Sulfate
Ce^{3+}	–	Cerium Ion
Cl	–	Chloride
Cs^+	–	Cesium Ion
Cu^+	–	Copper Ion
Fe^{2+}	–	Iron Ion
Ga^{3+},	–	Gallium Ion

H^+	–	Hydrogen Ion
k	–	Permeability in Darcy
K^+	–	Potassium
L	–	length of sample in cm
La^{3+}	–	Lanthanum Ion
Li^+	–	Lithium Ion
Na^+	–	Sodium Ion
Na_2O	–	Sodium Oxide
NH_3	–	Ammonia
NH_4^+	–	Ammonium Ion
Ni^{2+}	–	Nickel Ion
NO	–	Nitric Oxide
O	–	Oxygen
P	–	Phosphorus
P_2O_5	–	Phosphorus Oxide
Pt^{2+}	–	Platinum Ion
q	–	Flowrate in cm^3/sec
S	–	Sulfur
Si^{4+}	–	Silicate ion
SO_3	–	Sulfide
SO_4^{-2}	–	Sulfate ion
Sr^{+2}	–	Strontium ion
$SrSO_4$.	–	Strontium Sulfate
Zr	–	Zirconium
Zn^{2+}	–	Zink
ΔP	–	Pressure difference across the length, L
μ	–	Viscosity in centipoise

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Scaling is caused essentially by mixing incompatible fluids during well development operations, such as drilling, completion and workover, such as acidizing. Scaling associated with the enhanced recovery processes, such as water, alkaline water and carbon dioxide injection, may be caused by mixing incompatible fluids or pressure and temperature variations during the production of reservoir fluids (Civan, 2007).

Scale deposition is one of the most serious oil field problems that inflict water injection systems primarily when two incompatible waters are involved (Amer Badr et al., 2007a). Two waters are called incompatible if they interact chemically and precipitate minerals when mixed. In most cases, the scaled-up wells are causes by the formation of sulfate and carbonate scales of calcium and strontium. Because of their proportionate hardness and solubility, there are restricted processes available for their removal and preventive measures such as the squeeze inhibitor treatment must be taken (Amer Badr, 2008).

Zeolite can be classified as natural or synthetic zeolite. Zeolite has a rigid, three dimensional crystalline structure consisting of a network of interconnected channels and cages (Khairul Rozana, 2006). It is characterized by high specific surface areas and high cation exchange capacities (CECs) (Bowman, 2003). However, the synthetic zeolites have a wider range of properties and larger cavities than their natural counterparts compared to natural zeolite (Bell, 2001). In industry, zeolite is widely used in catalysis, adsorption and separation process.

1.2 Problem Statement

Inorganic scaling is a predominant formation-damage mechanism in most producing and injection wells worldwide. Scale deposition in the reservoir, in the hydrocarbon production wellbore penetrating the reservoir, and in surface and subsurface production equipment and tubing is typically caused by commingling incompatible fluids in situ and producing the resulting brine during hydrocarbon recovery operations, especially during enhanced oil recovery (EOR) operations involving waterflooding or water drive (Barthrope et al., 1994). Scale formation in surface and subsurface oil and gas production equipment has been recognized to be a major operational problem and a major cause of formation damage either in injection or producing wells (Amer Badr, 2008). Scale built-up decreases permeability of the formation, reduces well productivity and shortens the lifetime of production equipment (Collins et al., 2008). Basically, common hard scales are extremely resistant to both chemical and mechanical removal. Hence, in order to clean scaled-up wells and equipment it is often to shut down the production, move in workover rigs and pull the damaged tubing out of the well (Guimaraes et al., 2007). These activities are time-consuming and costly for the operation. In addition, it is desirable for oil well to get the maximum flow from the well and the build up of inorganic precipitates can slow flow rates, or even block flow rates in narrow tubing (Przybylinski et al., 2006). This obstruction of flow can be very undesirable.

In this project the synthetic zeolite has been chosen in mitigating inorganic scaling as it has noble characteristics; ion exchange capacity, large surface area and high absorbency (Halimatun, 2003). Synthetic zeolite possesses specific properties for specific applications plays a major role in industrial scale, in terms of petrochemical cracking, ion exchange (water softening and purification), separation and removal of gases and solvents, as well as molecular sieving (Rebecca, 2005). Thus, synthetic zeolite is believed to have the potential in mitigating inorganic scaling based on its characteristics and various applications in industry (Halimatun, 2003).

1.3 Objectives

1. To analyze the potential of synthetic zeolite in mitigating inorganic scaling.
2. To examine the changing in permeability of the rocks subjected to the fluid treated with synthetic zeolite.

1.4 Scope of Study

The scope of study in this project is to conduct literature review on inorganic scaling; its types and mitigating plans, characteristics of synthetic zeolite and its applications in industry, and permeability of the rock. The next step is to proceed with conducting experimental works and analysis as shown in Table 1.1. Finally, all the results obtained from the experimental works will be discussed and analyzed with reference to literature review.

Table 1.1: List of Experimental Works & Analysis

Experiment/Analysis	Purpose
Zeolite Ion Exchange Experiment	To study sorption of metal ions by synthetic zeolite.
Scanning Electron Microscope (SEM)	To examine morphology and crystal size of synthetic zeolite.
X-Ray Diffraction (XRD)	To analyze the mineralogy of synthetic zeolite before and after adsorption process.
X-Ray Fluorescence (XRF)	To identify chemical elements of barium and sodium in synthetic zeolite after adsorption process.
Permeability Test • Bench Top Permeability	To measure permeability of the core sample respected to the fluid treated with synthetic zeolite.

CHAPTER 2

LITERATURE REVIEW

2.1 Inorganic Scaling

Inorganic scaling is a process of deposition of scales from aqueous solutions of minerals, referred to as brines, when they become saturated as a result of the alteration of the state of their thermodynamic and chemical equilibrium (Civan, 2007). Scale deposition can occur from one type of water because of super-saturation with scales forming salts attributable to changes in the physical conditions under which the water exists. Scale can also deposit when two incompatible waters are mixed and super-saturation is reached (Amer Badr et al., 2007a).

The scale formation mechanisms can be classified as natural scaling and induced scaling. Natural scaling occurs mostly in the near production wellbore regions as a result of the liberation of dissolved light gases from the formation brine by high drawdown. Meanwhile, induced scaling occurs by mixing of formation brine with extraneous incompatible fluids invading the reservoir formation during drilling, cementing, completion, and workover operations (Civan, 2007). The scaling reaction depends on the concentrations of sulfate ions in the injected seawater and barium, strontium and calcium divalent cations in the formation brine to generate sulfate scale or bicarbonate and calcium ions to generate carbonate scale (Amer Badr et al., 2009; Jordan et al., 2008).

The use of seawater for pressure maintenance and oil recovery typically results in the problems with sulfate-scale deposition, which consists mostly of calcium and strontium (Ohen et al., 2004). Removal of these scales is in most cases complicated because the deposits are rarely pure calcium carbonate, calcium sulfate, barium sulfate, or strontium sulfate, but are usually a mixture of two or more of the inorganic components, corrosion products, organic scales, silica, and other impurities trapped in the inorganic lattice

(Ohen et al., 2004). Although a few cases have been reported of non water-producing oil wells that produced scales, typically oilfield scaling accompanies water production. Acid or any common solvent cannot easily remove some types of scales like barium sulfate, which readily incorporates radioactive radium in its structure (Ohen et al., 2004).

In addition, the injected seawater contains soluble salts such as sulfates and carbonates may be incompatible with the ions already contained in the oil-containing reservoir (formation water). The formation water may contain high concentrations of certain ions that are encountered at much lower levels in normal surface water, such as strontium, barium, zinc and calcium (Crossman et al., 2005). Partially soluble inorganic salts, such as barium sulfate and calcium carbonate, often precipitate from the production water as conditions affecting solubility, such as temperature and pressure, change within the producing well bores and topsides. This is especially prevalent when incompatible waters are encountered such as formation water, seawater or produced water.

In petroleum industry, brines are widely used in well completion as a kill fluid, completion fluid, packer fluid or workover fluid. During completion of the well, however, such brines may become lost in the reservoir and remain in the formation for a long period of time (Ke et al., 2007). If a reservoir contains hydrogen sulfide gas, or sulfur-containing chemical was used during the completion of the well, or a formation water contains sulfide ion, zinc sulfide or iron sulfide, scales can form when a zinc bromide brine is commingled with sulfide ion and where soluble iron is available as a result of corrosion (Ke et al., 2007). The formation of zinc sulfies scales can damage well productivity through a variety of problems such as plugging of flow channels in the formation and across the perforation, and scaling on downhole tool assembles and surface facilities (Ke et al., 2007).

2.1.1 Types and Treatment of Inorganic Scale

Basically, there are two main types of scales that are commonly found in the oil field; carbonate and sulfate scales (Ohen et al., 2004). Carbonate scale is caused by changes in the pressure and pH changes of the production fluid, while sulfate scale is mainly associated with the mixing of incompatible brines; formation water and injection water (Ohen et al., 2004). According to Amer Badr (2008), other less common scales have been reported are iron oxides, iron sulfate and iron carbonate, meanwhile, lead and zinc sulfide scale has also become a concern. Table 2.1 shows the major types of scale, along with their treatment strategies.

Table 2.1: Most Common Oilfield Scale (Amer Badr et al., 2007a)

Name	Origins	Primary Variable	Mitigation Strategies
Calcium Carbonate ($CaCO_3$)	• Originates from the nature of the reservoir itself. • Stimulated by the co-mingling of produced fluids from two or more different producing zones or reservoirs.	• Partial pressure of CO_2 • Temperature • Total dissolved salts • pH	• Dissolution by acidification • Application of calcium carbonate scale inhibitor
Calcium Sulfate: • Gymsum ($CaSO_4.2H_2O$) • Hemihydrate ($CaSO_4.1/2H_2O$) • Anhydrate ($CaSO_4$)	• Relatively soluble • Problem when conditions are close to the solubility limit and super-saturation occurs.	• pH • Temperature • Total dissolved salts • Pressure	• Using vinyl acetate-acrylic acid (VA-AA) and vinyl acetate-methacrylic acid (VA-MAA) copolymers.

Barium Sulfate ($BaSO_4$)	• Water incompatibility, primarily from seawater injection or seawater breakthrough • Co-mingling with produced water rich in barium. • Highly insoluble and will deposit at temperature drops across the production processing.	• Temperature • Pressure • Total dissolver salts	• Removal of sulfate ions from seawater for re-injection • Barium sulfate scale inhibitors or treatment with specialist dissolvers.
Strontium Sulfate ($SrSO_4$)	• Mixing of injected sea water and formation water that contained high concentration of strontium ion at various temperatures and pressures	• Temperature • Pressure • Total dissolved salts	• Removing sulfate in injected seawater
Iron Compounds: Ferrous Carbonate Ferrous Sulfide Ferrous Hydroxide	• Deposited-microbial enhanced corrosion • Reaction of iron oxide from corrosion and hydrogen sulfide, a by-product of sulfate reducing bacteria metabolism.	• Corrosion • Dissolved gases • pH	• Application of a specialist chelating and dissolution agent • Microbial control with biocide application.

This research is focusing more on barium sulfate scale. It is among the toughest scales to remove whether mechanically or chemically (Guimaraes, 2007). Thus, the alternatives to remediate this problem are often quite costly. According to Guimaraes (2007), there are some problems faced due to barium sulfate scale such as high cost mechanical techniques and chemical treatments (sometimes ineffective) must be used to cut through the scale blockages and HSE concerns arise regarding to radioactive waste disposal (Radium isotopes associated to barium sulfate scale). However, there are effective scale control methodologies for sulfate-based scale, such as seawater injection with scale inhibitor squeeze treatment to maintain production and sulfate reduction of the injection water; with or without the need to scale inhibitor (Jordan et al., 2008).

In the current study, there are different technologies have been developed to reduce the risk of scale formation, to control scale formation and to monitor treatment performance. Most currently available technologies are focused on use in the operational expenditure (OPEX) phase of field life (Jordan et al., 2008). However, evaluation of the scale risk and the combination of engineering and chemical solutions in the capital expenditure (CAPEX) phase can greatly improve the long-term field economics (Jordan et al., 2008). Tables 2.2 and Table 2.3 show currently available scale control, management and monitoring technology for subsea and platform application.

Table 2.2: Scale Control or Management Technology for Subsea and Platform Application (Jordan et al., 2008)

Technology	Descriptions
Squeeze Extenders	Mutual solvent chemicals used to enhance chemical adsorption and retention; also aid well clean up rates.
Oil-Soluble Scale Inhibitor	Scale inhibitor formulated with mutual solvent which give the aqueous formulation oil dispersible properties, thus eliminating any increase on near wellbore saturation (and also aids well clean up rates).
Gas Lift Deployed Scale Inhibitor	Aqueous or oil soluble scale inhibitor formulated such that it remains in the liquid phase when applied with gas lift gas.
Sulfate Removal	Nanofiltration of injection quality seawater results in reduced sulfate levels of between 40 to 120 mg/l.
Solid Inhibitor: • Rathole Deployed Scale Inhibitor • Reservoir Deployed Controlled Release Microparticles	 Solid scale inhibitor deployed into the rat hole of a production well. Microparticle of solid scale inhibitor that can be injected into the matrix of the reservoir.
Chemical Injection	Aqueous oil based scale inhibitor can be injected into the produced fluid via a capillary string run to the lowest packer.

Multifunctional Inhibitors	Scale inhibitor formulated with wax, hydrate, asphaltene, corrosion inhibitors to allow effective control of more than a single flow assurance problem (continuous injection).
Methanol Compatible Scale Inhibitors	Methanol miscible scale inhibitors that are not affected by methanol ingress from umbilical lines.
Scale Inhibitors for PWRI	Scale inhibitors that functional at low temperature to control sulfate scale and have a low adsorption on the reservoir.

Table 2.3: Scale Monitoring Technology for Subsea and Platform Application (Jordan et al., 2008)

Technology	Descriptions
Brine Analysis	10 ion analysis of principal ion such as Na, Mg, K, Ca, Sr, Ba, Fe, SO_4, HCO_3, Cl and organic acid plus gas phase CO_2, H_2S.
Residual Analysis	Scale inhibitor residual via ICP, wet chemical and tagging methods.
Thickness Sheer Mode Resonator (TSMR)	It works by changes in vibration frequency as a result of deposition of scale on the crystal surface.
Sensors: • pH, chloride ion • Ions	It suitable for downhole application that can measure the change in pH, chloride ions and specific scaling ions all allow the changes in water chemistry associated with injection water breakthrough to be monitored as well as the success of scale control program.
Pressure and Temperature	Sensor that can measure the change in downhole pressure and temperature to give indication of water breakthrough and also scale deposition causing flow restrictions.
Suspended Solids Monitoring via Environmental Scanning Electron Microscope/Energy Dispersive X-ray (ESEM/EDX)	Assessment of the amount, composition and texture of scale solids allows determination of effectiveness of scale control program.

2.1.2 Location – Oilfield Scale Form

According to Amer Badr (2008), scale precipitation from the injection water may occur behind the mixing zone as a consequence of temperature and pressure changes. Meanwhile, in the mixing zone, precipitation of soluble salts may occur due to the interaction, at local temperature and pressure of chemical contained in the injection water with chemical present in the reservoir brine. In addition, scale formation may also occur from seawater, aquifer, produced water re-injection (PWRI) and natural depletion (Amer Badr et al., 2009; Jordan et al., 2008).

Water injection, a long-standing practice in the oil industry is used to improve oil recovery. Pressure maintenance by water injection in some reservoirs may be considered for satisfactory oil recovery. The main objective of water-flooding is to place water into a rock formation at desired rate and pressure with minimal expense and trouble (Amer Badr et al., 2007b). In order to achieve this objective, the water should be treated and conditioned before injection. This treatment should solve problems associated with the individual injection waters, including suspended matter, corrosivity of water scale deposition and microbiological fouling and corrosion (Amer Badr et al., 2007b).

However, pressure and temperature decrease along the flow string up to the surface in the production well and further changes in thermodynamic conditions occur in the surface equipment, may also lead to the scale formation. Normally, these scales do the most damage in the well-bore when there are major falls in pressure but hardly any temperature changes (Amer Badr et al., 2007b). Refer Figure 2.1 to observe the changes which could produce scale at different locations during water injection.

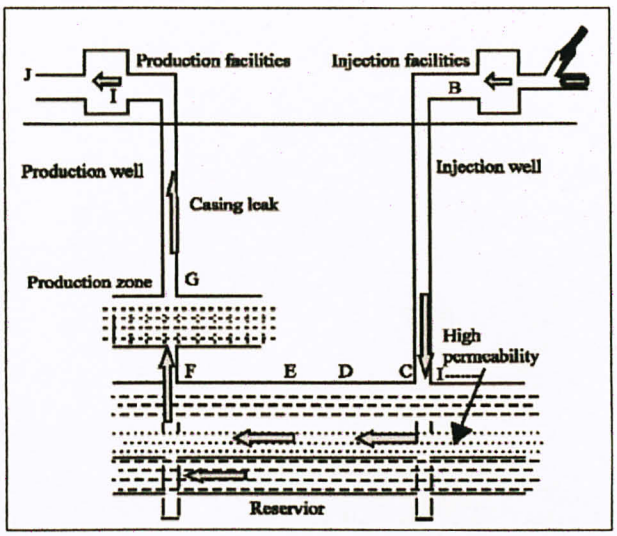

Figure 2.1: Produce Scale at Different Locations during Water Injection (Amer Badr et al., 2007b)

Location	Changes which could Produce Scale Formation
A to B	Mixing of brines for injection.
B to C	Pressure and temperature increase.
C to D	Pressure decline and continued temperature increase solution composition may be adjusted by cation.
D to F	Mixing of brines in the reservoir.
E to J	Pressure and temperature decline. Release of carbon dioxide and evaporation of water due to the pressure decline if a gas phase present or forms between these locations.
F	Mixing of formation water and injection water which has broken through at the base of the production well.
G	Mixing of brines produced from different zones.
H	Mixing of produced brine with brine from casing leak.

2.2 Zeolites

Zeolites are crystalline aluminosilicate with an open, three dimensional frameworks consisting of tetrahedral SiO_4^{4-} and AlO_4^{-5} units linked through shared oxygen in a continuous array, and contain cations water or other molecules within their pores (Kaur, 2005; Bell, 2001). Its microporous crystalline solids with well-defined structures are also known as molecular sieves referred to its crystalline structures. According to Wikipedia website, the maximum size of the molecular or ionic species that can enter the pores of a zeolite is controlled by the dimensions of the channels. Its porous structure also can accommodate a wide variety of cations, such as sodium, potassium, calcium and magnesium and others.

The rigid three-dimensional structures of zeolites make them free of the shrink or swell behavior associated with smectite clays (Bowman, 2003). For these reasons, zeolites can offer superior sorption and hydraulic properties and have found use as molecular sieves and sorbents in wastewater treatment. Zeolites have been particularly useful in removing cationic species such as ammonium and some heavy metals from water. High attrition resistance and CECs are positive attributes for such applications (Bowman, 2003).

2.3 Synthetic Zeolites

Synthetic zeolites have a wider range of properties and larger cavities than their natural counterparts compared to natural zeolite (Bell, 2001). Although some natural zeolites occur in large amounts, they offer only a limited range of atomic structures and properties compared to synthetic zeolite. In general, synthetic zeolites have large internal pore volumes, molecular-size pores, regularity of crystal structures, and the diverse framework chemical compositions allow "tailoring" of structure and properties (Sherman, 1999). Thus, highly active and selective catalysts as well as adsorbents and ion exchangers with high capacities and selectivities can be developed. In addition, many of the new synthetic zeolites had larger pore size than most of the known natural

zeolites, allowing applications involving larger molecules. In addition, many synthetic zeolites had larger pore volume, giving higher capacity (Sherman, 1999).

Moreover, many zeolites can be synthesized with SiO_2 higher or lower than in nature for the same framework type. Higher SiO_2 generally gives greater hydrothermal stability, stronger-acid catalytic activity, and greater hydrophobicity as adsorbents. Conversely, lower SiO_2 gives greater cation exchange capacity and higher adsorbance for polar molecules. Controlling the synthesis process optimizes a zeolite for different applications (Sherman, 1999).

2.3.1 Zeolite Socony Mobil-5 (ZSM-5)

ZSM-5 is a synthetic heterogeneous zeolite catalyst developed by Mobil Oil. It belongs to the three-letter zeolite structure code, MFI; pentasil family of zeolite. It is an aluminosilicate zeolite with high silica to alumina ratio. Generally, alumina is a hydrophilic material whereas silica rich zeolites are hydrophobic. Therefore, ZSM-5 is a hydrophobic material (Kaur, 2005). ZSM-5 has structures with two intersecting channel systems with 10-membered ring openings. They have porous structures and are thermally and acid stable. In ZSM-5 structures, the framework consists of one set of sinusoidal channels intersecting with straight channels, each with 10-membered ring openings. It has an average pore size of 0.63 nm (Kaur, 2005). Therefore, they are accessible to molecules with a diameter up to about 0.6nm. Figure 2.2 illustrate the ZSM-5 structure and the 10-ring MFI framework.

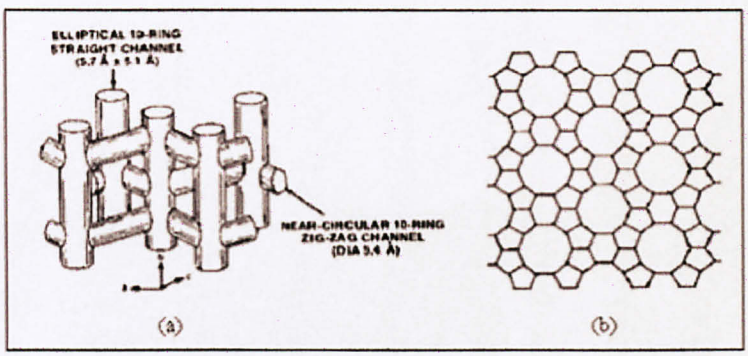

Figure 2.2: Structure of ZSM-5. (a) Channel system and (b) skeletal diagram of ZSM-5 layer (Kaur, 2005)

The shape and size of the pore system as well as the low aluminium context are responsible for the extraordinary catalytic and adsorption properties of these materials (Esemann, et al, 1996). Its structure is based on channels with insecting tunnels. The aluminium sites are very acidic. The substitution of Al^{3+} in place of the tetrahedral Si^{4+} silica requires the presence of an added positive charge (Harrison, 1997). When this is H^{+}, the acidity of the zeolite is very high. This acidity is used as a catalyst which has significant effect on reaction path and product distribution in reaction. The reaction and catalysis chemistry of the ZSM-5 is due to this acidity. Its chemical formula is $Na_nAl_nSi_{96-n}O_{192}\cdot 16H_2O$ ($0<n<27$).

ZSM-5 has been widely used as catalysts and sorbents in petroleum and petrochemical industry due to its unique shape selectivity, solid acidity, ion exchangeability, pore size, thermal stability and structural network (Shirazi et al., 2008). The catalytic and sorption properties of the zeolite are often influenced by their crystal size. The physicochemical properties of ZSM-5 zeolite is influenced by chemical composition and nature of the reagents, alkalinity, template, temperature, time of crystallization, water contents and other factors such as ageing and stirring (Shirazi et al., 2008).

According to the important role of surface area and diffusional path in the catalytic behavior, zeolites with small crystal size having high external surface area and short diffusional path can have significant effect on product distribution in catalytic reaction (Shirazi et al., 2008). The morphology, crystal size distribution and Si/Al in the zeolite structure are influenced by different variables such as initial chemical composition, the silicon and aluminum source, the alkalinity, the presence of seeds, the OH/SiO_2 molar ratio and dynamic of the system (Shirazi et al., 2008). Table 2.4 shows some of the studies regarding on ZSM-5 ion exchange.

Table 2.4: List of Several Studies Regarding on ZSM-5 Ion Exchange

Type of Zeolite	Cation Exchange	Purpose	Reference
ZSM-5	Ce^{3+}	Synthesis and Characterization of Ce-ZSM-5 Zeolite Membranes	Cheng et al. (2006)
ZSM-5	Cu^{+} and Cu^{2+}	Nature of Copper Active Sites in CuZSM-5: Theory and Experiment	Broclawik et al. (2002)
ZSM-5	Fe^{2+}	Fe-ZSM-5 for Selective Catalytic Reduction of NO with NH_3: A Comparative Study of Different Preparation Techniques.	Long et al. (2001)
ZSM-5	Ba^{2+}, Al^{3+}, La^{3+}	Acidic Properties of ZSM-5 Zeolite modified with Ba^{2+}, Al^{3+} and La^{3+} ion-exchange	Tynjala et al. (1996)
ZSM-5	Cs^{+}, Ba^{2+}	Exploring Cation Siting in Zeolite ZSM-5 by Infrared Spectroscopy, EXAFS and Computer Simulations.	Esemann et al. (1996)
H-ZSM-5	Ga^{3+}, Zn^{2+}, Pt^{2+}	Study on Non-Oxidative Reactions of Propane on Zn/Na-ZSM5	Biscardi et al. (1999)
NH_4-ZSM-5	Na^{+}, K^{+} and Li^{+}	Ion Exchange properties of ZSM-5	Bhatia S. (1990)

Selectivity Series
Monovalent ions : $Cs^{+} > NH_4^{+} > K^{+} > Ag^{+} > Na^{+} > Li^{+}$
Divalent ions : $Cu^{2+} > Zn^{2+} > Ni^{2+}$

Figure 2.3: Selectivity Series for Ion Exchange in NH_4-ZSM-5 (Bhatia S., 1990)

2.4 Application of Zeolites In Industry

Zeolites are widely used as ion-exchange beds in domestic and commercial water purification, softening, and other applications (Halimatun, 2003). In chemistry, zeolites are used for separation, catalytic and adsorption process.

2.4.1 Common Application of Zeolites

There are three main applications of zeolites in industry; catalysis, adsorption and separation, and ion exchange (Bell, 2001):

Catalysis

Zeolites have the ability to act as catalysts for chemical reactions which take place within the internal cavities. An important class of reactions is that catalyzed by hydrogen-exchanged zeolites, whose framework-bound protons give rise to very high acidity. This is exploited in many organic reactions, including crude oil cracking, isomerization and fuel synthesis. Zeolites can also serve as oxidation or reduction catalysts, often after metals have been introduced into the framework.

Adsorption and Separation

The shape-selective properties of zeolites are also the basis for their use in molecular adsorption. The ability preferentially to adsorb certain molecules, while excluding others, has opened up a wide range of molecular sieving applications. Sometimes it is simply a matter of the size and shape of pores controlling access into the zeolite. In other cases different types of molecule enter the zeolite, but some diffuse through the channels more quickly, leaving others stuck behind, as in the purification of para-xylene by silicalite.

In addition, the cation-containing zeolites are extensively used as desiccants due to their high affinity for water, and also find application in gas separation, where molecules are differentiated on the basis of their electrostatic interactions with the metal ions. Conversely, hydrophobic silica zeolites preferentially absorb organic solvents. Zeolites can thus separate molecules based on differences of size, shape and polarity.

Ion exchange

The loosely-bound nature of extra-framework metal ions means that they are often readily exchanged for other types of metal when in aqueous solution. This is exploited in

2.4.1 Common Application of Zeolites

There are three main applications of zeolites in industry; catalysis, adsorption and separation, and ion exchange (Bell, 2001):

Catalysis

Zeolites have the ability to act as catalysts for chemical reactions which take place within the internal cavities. An important class of reactions is that catalyzed by hydrogen-exchanged zeolites, whose framework-bound protons give rise to very high acidity. This is exploited in many organic reactions, including crude oil cracking, isomerization and fuel synthesis. Zeolites can also serve as oxidation or reduction catalysts, often after metals have been introduced into the framework.

Adsorption and Separation

The shape-selective properties of zeolites are also the basis for their use in molecular adsorption. The ability preferentially to adsorb certain molecules, while excluding others, has opened up a wide range of molecular sieving applications. Sometimes it is simply a matter of the size and shape of pores controlling access into the zeolite. In other cases different types of molecule enter the zeolite, but some diffuse through the channels more quickly, leaving others stuck behind, as in the purification of para-xylene by silicalite.

In addition, the cation-containing zeolites are extensively used as desiccants due to their high affinity for water, and also find application in gas separation, where molecules are differentiated on the basis of their electrostatic interactions with the metal ions. Conversely, hydrophobic silica zeolites preferentially absorb organic solvents. Zeolites can thus separate molecules based on differences of size, shape and polarity.

Ion exchange

The loosely-bound nature of extra-framework metal ions means that they are often readily exchanged for other types of metal when in aqueous solution. This is exploited in

a major way in water softening, where alkali metals such as sodium or potassium prefer to exchange out of the zeolite, being replaced by the "hard" calcium and magnesium ions from the water. Many commercial washing powders thus contain substantial amounts of zeolite. Commercial waste water containing heavy metals, and nuclear effluents containing radioactive isotopes can also be cleaned up using such zeolites.

2.4.2 Zeolite Membranes

Zeolite membranes have been used for pervaporation both industrially and laboratory studies. Zeolite membranes have uniform, molecular-sized pores, and they separate molecules based on differences in molecules' adsorption and diffusion properties. It is well suited for separating liquid-phase mixtures by pervaporation and it has been used for dehydrating organic compounds, remove organics compound from water, separate organic mixtures and remove water form acid solutions on the laboratory scale (Falconer et al., 2004). Pervaporation allows separations of some mixtures that are difficult to separate by distillation, extraction and sorption. Zeolite membranes are polycrystalline zeolite layers deposited on porous inorganic supports and they offer several advantages over polymeric membranes (Falconer et al., 2004):

- Zeolite membranes do not swell, whereas polymeric membranes do.
- Zeolites have uniform, molecular-sized pores that cause significant differences in transport rates for some molecules, and allow molecular sieving in some cases.
- Most zeolite structures are more chemically stable than polymeric membranes, allowing separations of strong solvents or low pH mixtures.
- Zeolites are stable at high temperature (as high as 1270 K for some zeolite).

Even though, zeolite membranes in general cost significantly more to produce than polymer membranes, but their advantages make zeolites attractive alternatives for separating mixtures whose components have adsorption or size differences, but are difficult to perform using polymeric membranes and other conventional separations methods.

2.5 Application of Synthetic Zeolites in Industry

2.5.1 Zeolite Socony Mobil-5 (ZSM-5)

In petroleum industry, ZSM-5 is used for hydrocarbon inter-conversion (as a heterogeneous catalyst for hydrocarbon isomerization reactions). An example use is in the isomerization of xylene- from meta to para-xylene. The acidic zeolite promotes carbocation isomerizations. There are two suggested mechanisms for this type of isomerizations (Harrison, 1997). Firstly, shape may play a role. Perhaps para-xylene has a shape which allows it to diffuse rapidly through the zeolite structure, whereas as meta-xylene takes longer to pass through the zeolite and thus has more opportunity to be converted into the para-xylene. Secondly, is that the orientation of reactive intermediates within the zeolite channels favors specifically para-xylene. Table 2.5 shows some other applications of ZSM-5 in industry.

Table 2.5: Some Large-Scale Processes Based on Zeolite Catalysts (Bhatia S., 1990)

Type of zeolite	Process	Objective	Main Process Characteristic
ZSM-5	M-forming	High yield, octane number (ON) increase in gasoline	Cracking depends on degree of branching
	Xylene isomerization	High yield *p*-xylene production	High through-put, long cycle
	Toluene disproportionation	Benzene and xylenes from toluene	Suppression of side reaction
	Methanol to gasoline	Methanol (from coal or natural gas) conversion to high scale grade gasoline	Synthesis of hydrocarbon on restricted to gasoline range (C4 to C10) including aromatics
Ni-ZSM-5	Dewaxing	Liquid fuel from heavy fuel oil; lube oil with low pour points	Cracking high molecular weight n-monomethyl paraffins

2.5.2 Surfactant Modified Zeolite (SMZ-5)

SMZ-5 is used for environmental applications particularly for the removal of contaminants from water (Bowman, 2003). SMZ-5 is capable of simultaneous sorption of anions, cations and non-polar organic molecules from water and it was also has been tested as a sorbent for organics present in oilfield wastewater (Bowman, 2003).

Purification of Produced Water Treatment

Purification of produced water by zeolite membranes is a novel technology used for reclamation of produced water for beneficial used. Because of extremely stable chemical, mechanical and thermal properties, zeolite membranes show greatest advantages in difficult situation such as operations in a strong solvent environment or those requirement high pressures (Li et al, 2007).

According to the research done by Petroleum Recovery Research Center (PRRC), Mexico, in 2003, the synthetic zeolite membranes (Polycrystalline Zeolite Membranes) has shown 90% of salt rejection rate of 80,000 ppm produced water (Li et al., 2003). Their research is focusing in high-salinity produced water and brine treatment. The percentage of salt rejection based on specific ions metals has shown in Figure 2.4. In addition, the synthetic zeolites membranes also have high thermal and chemical stability, high flux and has regeneration capability (Li et al., 2003).

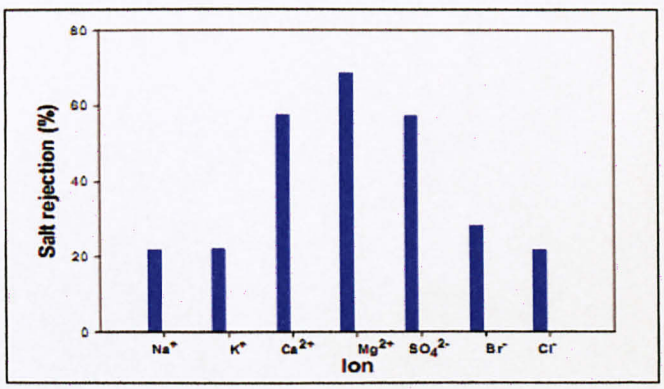

Figure 2.4: Graph of Salt Rejection (%) versus Metal Ions (Li et al., 2003)

Treatment of Produced Water Using a SMZ/Vapor Phase Bioreactor System (Katz et al., 2005)

The objectives of developing this treatment system is for removing hazardous organic contaminants from produced water; from petroleum, natural gas, coalbed methane and also to remove BTEX (Benzene, Toluene, Ethylbenzene, and Xylenes). It is also to develop low cost system at wellhead or treatment facility and also to obtain water that is ready for desalination (Katz et al., 2005). This treatment has been used in remove BTEX from produced water and regeneration and off-gas treatment. This research can be examining several industries for potential application in power industry (process water), and oil and gas industry (cementing).

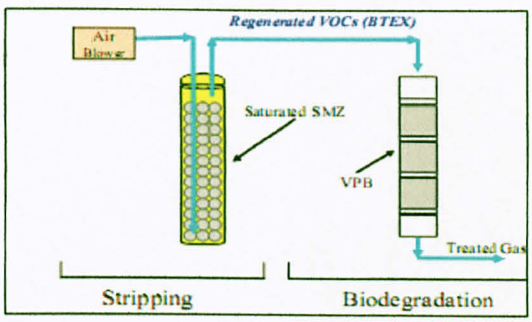

Figure 2.5: Regeneration and Off-gas Treatment (Katz et al., 2005)

SMZ Permeable Reactive Barriers (Bowman, 2003)

SMZ is use in subsurface permeable reactive barriers (PRBs). The objective of PRBs is to install a reactive material in the path of a groundwater contamination plume. The contamination is treated in situ, eliminating the expense and disposal problems associated with ex situ technologies such as pump and treat (Bowman, 2003). The ability of SMZ to adsorb a wide range of contaminants, its high permeability, and its low unit cost makes is attractive for PRB applications (Bowman, 2003).

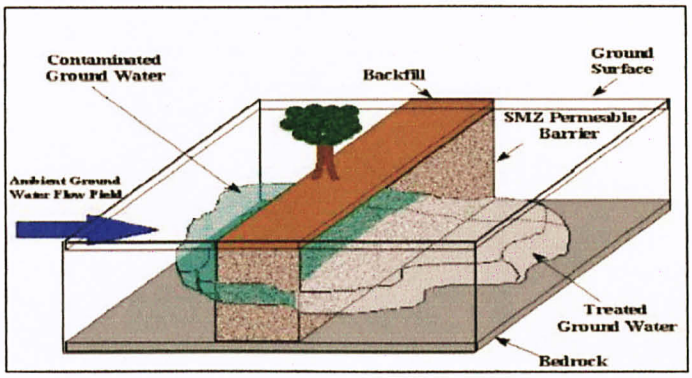

Figure 2.6: Concept of a Subsurface PRB for Treating Contaminated Groundwater (Bowman, 2003)

2.6 Permeability

Permeability is a property of porous media that measures the capacity and ability of the formation to transmit fluids. The rock permeability is a very important rock property because it controls the directional movement and flow rate of the reservoir fluids in the formation (Tarek, 2001). Formations that transmit fluids readily, such as sandstones, are described as permeable and tend to have many large, well-connected pores. Impermeable formations, such as shales and siltstones, tend to be finer grained or of a mixed grain size, with smaller, fewer, or less interconnected pores (Schlumberger, Oil Glossary). Permeability plays the importance role in determining the flow characteristics of hydrocarbons in oil and gas reservoirs, and of groundwater in aquifers. The Darcy's Law is used in defining permeability in terms of measurable quantities.

$$q = -\frac{kA}{\mu}\frac{\Delta P}{L} \qquad (2.1)$$

Where q = flowrate in cm^3/sec

A = cross sectional area of flow in cm^2

ΔP = pressure difference across the length, L

μ = viscosity in centipoise

L = length of sample in cm

k = permeability in Darcy

Basically, there are two phenomena can change the permeability of the rock (Amer Badr, 2008). One is the changing of porosity. This phenomenon is due to the swelling of clay minerals or deposition of solids in the pore body. The other is plugging of pore throats. The narrow passages govern the ease of fluid flow trough porous media. If there are blocked, the permeability of the porous will be low even though the pore space remains large.

2.6.1 Types of Permeability

Basically, there are three types of permeability; absolute permeability, effective permeability and relative permeability (Schlumberger, Oil Glossary). Absolute permeability is the measurement of the permeability conducted when a single fluid, or phase, is present in the rock. Meanwhile the effective permeability is the ability to preferentially flow or transmit a particular fluid through a rock when other immiscible fluids are present in the reservoir (for example, effective permeability of gas in a gas-water reservoir). The relative saturations of the fluids as well as the nature of the reservoir affect the effective permeability. Finally, the relative permeability is the ratio of effective permeability of a particular fluid at a particular saturation to absolute permeability of that fluid at total saturation. If a single fluid is present in a rock, its relative permeability is 1.0. Calculation of relative permeability allows for comparison of the different abilities of fluids to flow in the presence of each other, since the presence of more than one fluid generally inhibits flow.

2.6.2 Permeability Reduction

In petroleum industry, produced water re-injection (PWRI) is one of the viable methods to manage the large amount of water produced from oil recovery operations. However, permeability reduction caused by the particles being retained within porous formations is a major problem affecting the effectiveness of the process (Wong et al., 2009). The permeability reduction is correlated with the amount of particles retained within the

specimen independent of the injected influent concentration, injected velocity, injected fluid volume and particle deposition profile (Wong et al., 2009).

Moreover, the permeability reduction can also occur at the cross-flow microfiltration in polymeric membranes. Polymeric membranes is widely used as a final refining step in commercial processes for drinking water production, wastewater treatment, food processing, pharmaceutical industry, biotechnology and biomedicine (Seminario et al., 2002). However, membrane fouling inherent to the operation, remains a restriction. During cross-flow microfiltration suspended particles are transported and eventually capture at the membrane surface causing a drastic increase of local concentration of pollutant particles, gradual fouling and consequent permeability reduction (Seminario et al., 2002).

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

The process flow of the research starts with analyzing background study of the project and identifies problem statement. Next, the objectives that need to be achieved at the end of the project were set and the scope of study was determined. Then, the process flow continues with developing project scheduling and project planning for ease management of the project. In project planning, all sorts of activities and experiments needed for this project have been identified. Then, for the project scheduling, the key milestones and Gantt chart have been determined in order to make sure all the activities are on the right track.

3.2 Project Activities

In project activities, some project planning and experimental works have been planned for this project (refer to Figure 3.1).

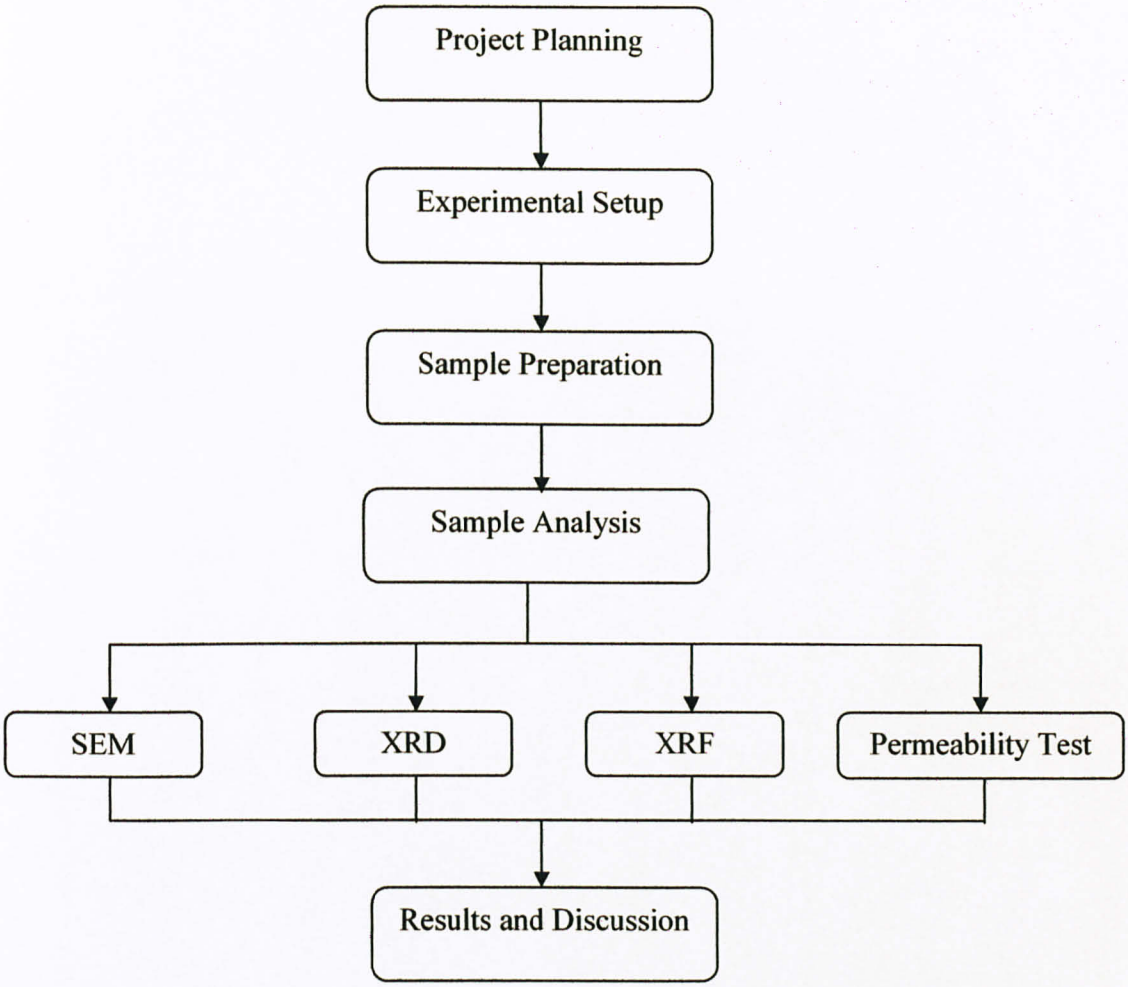

Figure 3.1: Process Flow of Project Activities

3.2.1 Zeolite Ion Exchange Experiment (Sample Preparation)

The main purpose of this experiment is to study the sorption of metal ion by synthetic zeolite. In this experiment, barium sulfate scale has been used as inorganic scaling. Basically, the barium sulfate scales can be formed by mixing the barium chloride and sodium sulfate solution; $BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaCl(aq)$. Next, the samples from this experiment are used for XRD and XRF analysis, and also being used for permeability test.

The procedure of zeolite ion exchange experiment is as follows:

1. 25 grams of synthetic zeolite (ZSM-5) is weighted and placed into a mesh.
2. 1.779 grams of barium chloride is weighted and placed into 2.0 liters beaker and 1 liter of deionized water is added.
3. The barium chloride and deionized water are stirred until all the barium chloride dissolved.
4. Pump is placed into the 2.0 liter beaker containing barium chloride aqueous solution.
5. Then, the mesh containing synthetic zeolite is placed at the top of the 2.0 liters beaker.
6. Next, the pump is on in order to let the barium chloride aqueous solution circulated through the zeolite for one day.
7. Step 1 to 6 is repeated by using 6.178 grams of sodium sulfate.

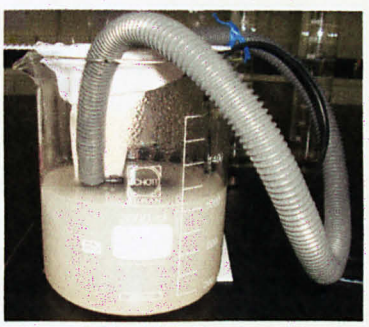

Figure 3.2: Setup for Zeolite Ion Exchange Experiment

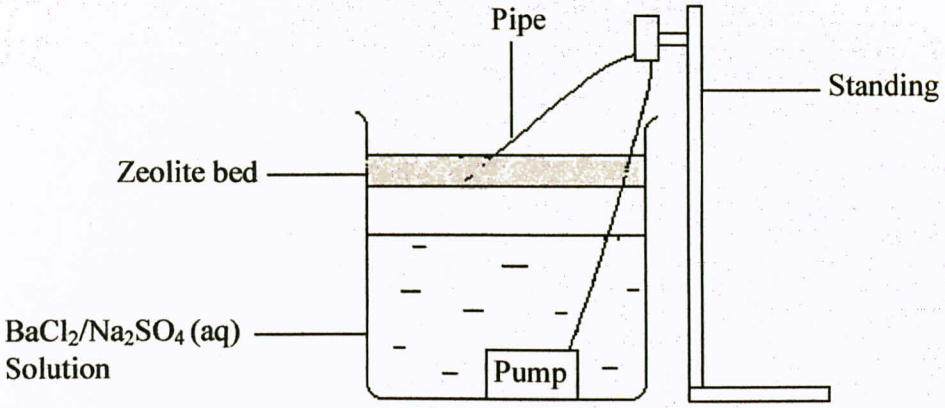

Figure 3.3: Schematic Diagram for Zeolite Ion Exchange Experiment

3.2.2 Permeability Test

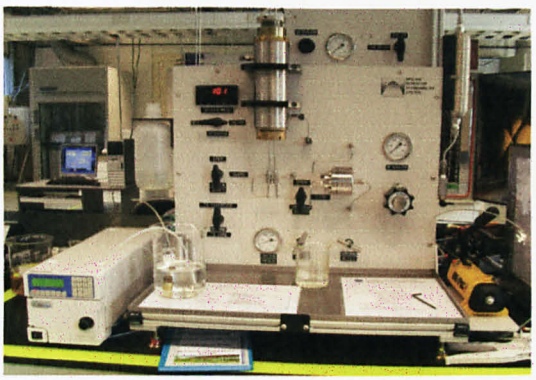

Figure 3.4: Bench Top Permeability System

Bench Top Permeability System is used to measure the permeability of the saturated core. In this project, the effective permeability of the core will be measured before and after the core being saturated with the sample solution. Before running the experiment, some of the parameters need to be determined; which are diameter and length of the core, the viscosity of the liquid used and initial flow rate. In this experiment, initial flow rate of 1.5ml/min and 1000psi confining pressure. Refer Figure 3.5 for Process Flow Diagram for Bench Top Permeability.

Core Sample Preparation

The following are procedures of core sample preparation before running the experiment:

1. The length and diameter of the core sample is measured by using digital calipers.
2. Next, the porosity of the core sample is determined by using PoroPerm System. From this equipment, bulk volume, porosity and grain volume of the core are taken.
3. Then, the core is saturated with the sodium sulfate in desiccators for 1 day.
   Note: In desiccators, a vacuum was drawn on the core sample for 12 hours to remove air from the core.
5. Step 1 to 3 is repeated by using the second core and the core is saturated by using barium chloride.

Operating Procedures for Bench Top Permeability System

Setup and operating procedures for Bench Top Permeability System have been divided into three parts, which are filling the confining system with hydraulic fluid, loading a core sample in the core holder and finally measuring liquid permeability.

Part 1: Filling the confining system with hydraulic fluid

1. The confining isolate and the confining bleed valves located on the front panel of the BPS-805 are closed.
2. The confining isolate valve on the panel is opened.
3. The confining fluid from the pump is pump slowly to the core holder until confining pressure reached to 1000psi.
4. The confining isolate valve on the panel is closed.

Part 2: Loading a core sample in the core holder

1. The saturated core sample is inserted in the downstream end of the holder.
2. The core sample is flow with the downstream and piece with spacer and downstream cap end.

3. The downstream end cap is screwed all the way on while aligning the outlet tubes with the two 1/8 bulkhead fittings on the front panel.
4. The upstream end piece is inserted with the appropriate space into the core. Note: Make sure the spacer is properly aligning on the end piece.
5. Guide the axial nut gently over the inlet tube fittings.
6. The confining bleed valve is closed.
7. The confining isolate valve is opened.
8. The confining fluid system is pumped to 1000psi confining pressure.
9. The confining isolate valve is close.
10. The fittings are connected to the inlet and outlet tubes.

Part 3: Measuring liquid permeability

1. After loading the core sample and confining pressure on the core sample, the dP transducer bypass valve is set to the bypass position.
2. The delta-P transducer indictor is set to zero by the pressing the '>/TARE' button on the display meter.
3. Once the flow is stabilized, the upstream pressure is monitored.
4. The stable delta-P value is recorded.
5. The pump is stopped.
6. The core sample is unloaded.
7. The core holder annulus and flow tubing are cleaned.

Core Flooding Procedure

There are two core samples used in this experiment, one is to be saturated with sodium sulfate solution and other is to be saturated with barium chloride solution. The following are the procedures for core flooding:

1. The core sample is placed into the core holder.
   Note: This core sample is already saturated with sodium sulfate in desiccators.
2. The sodium sulfate solution is injected into core sample and its initial permeability is taken.
3. Then, the barium chloride solution (treated/untreated with synthetic zeolite) is injected into the core sample.
4. Finally, the sodium sulfate solution is injected again into the core sample for final permeability measurement.
5. Step 1-5 is repeated by using second core sample; barium chloride solution is used to saturate the core, and sodium sulfate solution (treated/untreated) is injected into the core sample.

3.3 Tool

Table 3.1 shows the equipments used for the experimental work and analysis during this project.

Table 3.1: List of Equipments

Tools	Purposes
Scanning Electron Microscope (SEM)	To examine morphology and crystal size of synthetic zeolite.
X-Ray Diffraction (XRD)	To analyze the mineralogy of synthetic zeolite before and after adsorption process.
X-Ray Fluorescence (XRF)	To identify chemical elements of barium and sodium in synthetic zeolite after adsorption process.
Bench Top Permeability	Measure effective permeability of core sample.

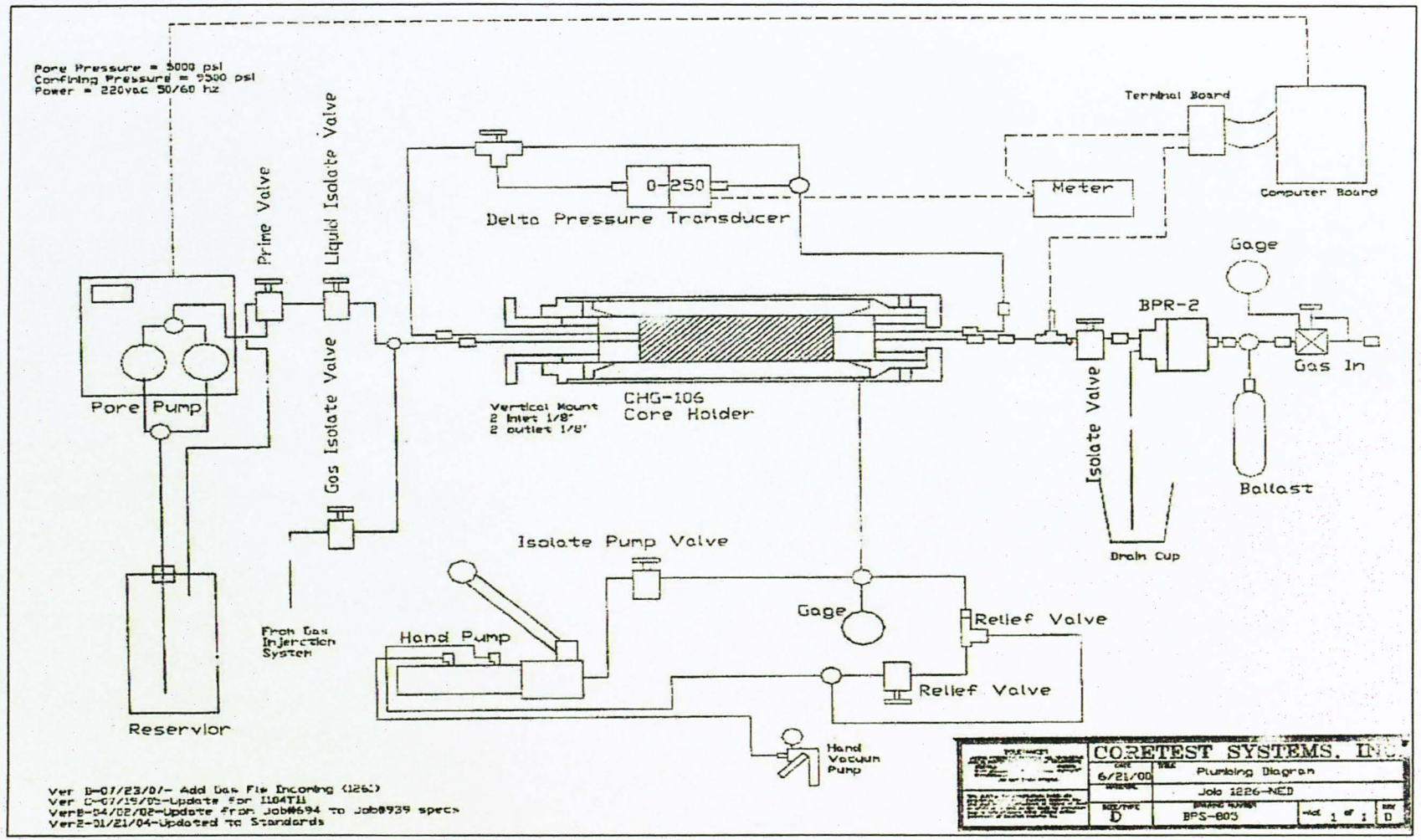

Figure 3.5: Process Flow Diagram for Bench Top Permeability System

3.4 Key Milestones

No.	Detail/Week	1	2	3	4	5	6	7	8	9		11	12	13	14	15
1	Project Work Continue															
2	Submission Progress Report 1															
3	Project Work Continue															
4	Submission Progress Report 2															
5	Seminar															
6	Project Work Continue															
7	Poster Exhibition															
8	Submission of Dissertation (Soft Bound)															
9	Oral Presentation															
10	Submission of Project Dissertation (Hard Bound)															

Mid-Semester Break

Suggested Milestone
Process

3.5 Gantt Chart

No.	Detail/Week	Duration	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov
1	Literature Review	4 months						Semester Break					
2	Analysis	4 months											
3	Methodology	3 months											
4	Result and Discussion	2 months											
5	Conclusion and Recommendation	2 months											
6	Poster Exhibition	1 month											
7	Final Report	2 months											
8	Oral Presentation	1 month											

Process

CHAPTER 4

RESULT AND DISCUSSION

This chapter consists of the results obtained and analyzed from the experiments done during this project; zeolite ion exchange experiment and permeability test. The results obtained are analyzed and discussed in four sections which are; examine morphology of ZSM-5 using SEM, analyzed mineralogy and chemical element of ZSM-5 before and after ion exchange process using XRD and XRF respectively, and permeability test using Bench Top Permeability System.

4.1 Morphology of ZSM-5

In this section, Scanning Electron Microscope (SEM) is used to examine the morphology of the synthetic zeolite, ZSM-5. The type of ZSM-5 used in this project is NH_4-ZSM-5, with Silica/Aluminum (Si/Al) molar ratio of 40. The Si/Al ratio is really important as it can affect the crystal size and surface area of the zeolite. According to Shirazi et al., (2008), the crystal size and surface area are increasing as the Si/Al molar ratio is increases. However, zeolite with small crystal size is having high external surface area and short diffusional path. Figure 4.1 shows the morphology of ZSM-5 crystals. It has a very uniform size distribution and do not contain amorphous substances or other crystalline impurities.

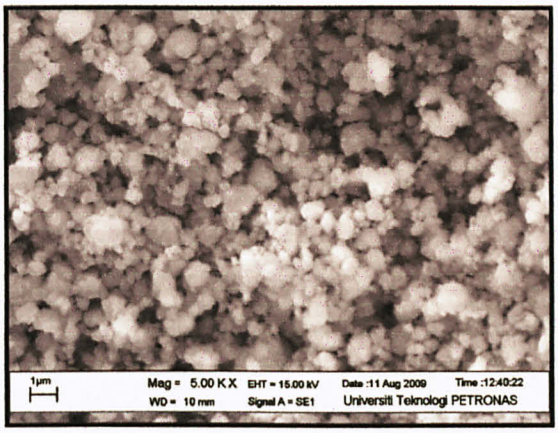

Figure 4.1: SEM Image of ZSM-5

4.2 Mineral Composition

X-Ray Diffraction (XRD) has been used to analyze mineral composition of ZSM-5 before and after adsorption process. Generally, XRD is widely used for identification of unknown crystalline materials such as minerals and inorganic compound. It is also used to determine degree of crystallinity of the material and possibility of other crystalline impurities. Thus, this analysis can be used to confirm the structure and crystallinity of ZSM-5. Based on the result obtained from XRD, ZSM-5 has orthorhombic crystal system with lattice parameters of a=20.104, b=19.897 and c=13.395. All three bases intersect at 90° angles.

Figure 4.2 shows the comparison of XRD patterns for ZSM-5 before and after adsorption process. Figure 4.2 (a) shows the XRD pattern for ZSM-5 before adsorption process. Meanwhile, Figure 4.2 (b) and (c) shows the XRD patterns for ZSM-5 after adsorption process with barium chloride and sodium sulphate respectively. Based on the result obtains in Figure 4.2, the ZSM-5 before the ion exchange experiment has higher peak intensity which it indicates higher crystallinity compared to the ZSM-5 after the adsorption process.

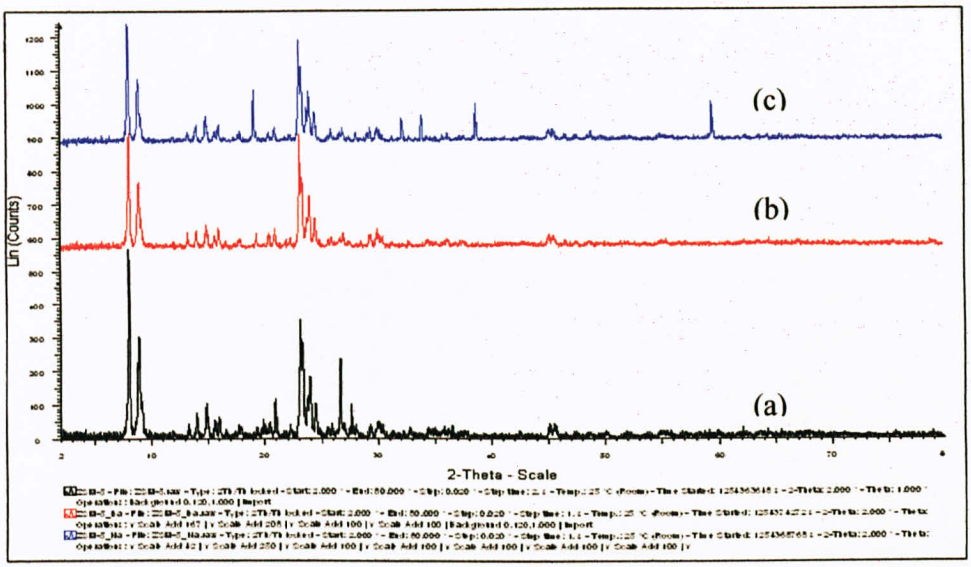

Figure 4.2: Comparison of Mineralogy of ZSM-5 Before and After Adsorption Process: (a) ZSM-5 (base); (b) Ba-ZSM-5; (c) Na-ZSM-5

According to Khairul Sozana (2006), the cation exchange process leads to rearrangement of other ions in zeolite structure. When one cation replace to other cations, it will causes changes in local distributions and electrostatic fields. The changes then may cause an alteration of the framework, leading to shifting of the diffraction peaks. This has been shown in Figure 4.2 (c), whereby there are some shifted of the peaks towards high angle, when ZSM-5 is run through the sodium sulfate solution. In addition, as mentioned in Chapter 3, the zeolite ion exchange process is started with the barium chloride and then followed by sodium sulfate ion exchange. Thus, it has shown that the exchanging cations for example barium with other metal ions having cationic size smaller such as sodium than will result in increasing the intensities of the respective peaks.

4.3 Elemental Analysis

In this analysis, X-Ray Fluorescence (XRF) has been used to determine chemical elements of ZSM-5 before and after adsorption process. XRF can measure all the elements in the periodic table qualitatively, semi-quantitatively and quantitatively in powders, solids and liquid. It has high accuracy and its typical limits of detection are from 0.1 to 10 ppm (Schlotz et al., 2006). Thus, the total percentage of all elements might

not be 100 percent because of this limitation. The result for this analysis is shown in Table 4.1.

Table 4.1: Chemical Elements of ZSM-5

Element	ZSM-5 (%)	Ba-ZSM-5 (%)	Na-ZSM-5 (%)
O	53.00	52.00	52.00
Al	1.03	0.99	0.93
Si	45.28	44.24	41.13
P	0.41	0.42	0.40
Ca	0.13	0.12	0.12
Fe	0.04	0.04	0.03
Na	-	-	2.07
S	-	-	2.22
Zn	-	-	0.00
Zr	-	-	0.01
Ba	-	1.78	0.69
Cl	-	0.25	-
Total	**99.89**	**99.82**	**99.59**

Based on the literature review, ZSM-5 is an aluminosilicate zeolite with high silica to alumina ratio, thus it should have high percentage or amount of silica in its composition. This has been proved from this analysis, whereby, ZSM-5 has higher percentage of silica which is 45.28% compared to alumino which is only 1.03% (refer Table 4.1). Zeolite rich in silica is categorized as a hydrophobic material. This hydrophobic property can remove a variety of dissolved organic compounds from water (Halimatun, 2003).

Moreover, the ability of ZSM-5 in mitigating inorganic scaling can also be determined by observing chemical elements of ZSM-5 before and after adsorption process. Before the zeolite ion exchange process, there are no traces of barium and sodium elements in ZSM-5 composition. However after barium chloride has been run through the zeolite, there are some traces of barium which is 1.78% and small amount of chloride which is 0.25% have

been adsorb by ZSM-5. In addition, there are also some traces of sodium which is 2.04% and sulfur which is 2.22% has been found in ZSM-5 composition after the zeolite ion exchange with sodium sulfate.

Table 4.2 shows oxide compounds found in ZMS-5. This result is also obtained from XRF since it can also detect the oxide compound in materials such as calcium oxide and sodium oxide. Based for the result, there are traces of sulfide (SO_3) found in ZSM-5 which is 1.39%. However, supposedly the sulfate compound (SO_4) is found or adsorb by ZSM-5.

Table 4.2: Oxide Compound in ZSM-5

Compound	ZSM-5 (%)	Ba-ZSM-5 (%)	Na-ZSM-5 (%)
SO_3	-	-	1.39
CaO	-	-	0.17
Al_2O_3	-	1.41	-
Na_2O	1.40	-	-
P_2O_5	0.94	-	-

From Table 4.1, the percentage of sodium adsorb by ZSM-5 is a little bit higher compared to barium. This is probably because of the effect of ZSM-5 structure. According to Bhatia, S. (1990), ZSM-5 is not readily susceptible to ion exchange due to the hindrance from bulky quaternary cations in its channel system. Incoming and outgoing ions all have to pass through the channels in order to complete the ion exchange process. Therefore, in order to obtain the ion exchange information, these bulky organics must be removed and replaced by smaller cations. In addition, the zig-zag channels of ZSM-5 may encounter some problems at the intersection since any deposition could either partially or fully obstruct the diffusion. Thus, affect the adsorption of adsorbates even though the zeolite has three dimensional pore systems Therefore, the sodium ion is easily to be adsorbed by the ZSM-5 since it is the smaller cations compared to barium ion. Thus, this analysis has shown that ZSM-5 does have the ability to adsorb the barium and sodium elements, but also some of the chloride and sulfur elements.

4.4 Permeability Test

The objective of this experiment is to examine the changing in permeability of the core samples subjected to the fluid treated with synthetic zeolite. There are four sample solutions have been used for this test; barium chloride (treated and untreated) and sodium sulfate (treated and untreated). In this test, Bench Top Permeability System is used to measure effective permeability of the core samples.

4.4.1 Characteristics of Core Samples

Before running the Bench Top Permeability System, the dimension and characteristics of the core samples need to be determined first. The dimension and weight of the core samples are measured by using digital caliper and electronic balance (refer Table 4.3). Next, the porosity, pore volume and grain volume have been determined by using Poroperm equipment (refer Table 4.4).

Table 4.3: Dimension and Weight of the Core Sample

	Core 1	Core 2
Length (mm)	42.95	38.98
Diameter (mm)	38.02	37.98
Weight (g)	90.17	94.38

Table 4.4: Characteristics of the Core Samples

	Core 1	Core 2
Porosity (%)	27.83	20.32
Pore volume (cc)	12.90	8.93
Grain Volume (cc)	33.45	35.01

From Table 4.4, the porosity of Core 1 is 27.83% and Core 2 is 20.32%, typically the values of porosity between 20-35% are considered as consolidated sandstone.

4.4.2 Effective Permeability of the Core Sample

In permeability test, the treated aqueous solution is the sample solution that has been circulated through zeolite bed. Then, this aqueous solution is injected into the core sample, as mentioned in Chapter 3. Table 4.5 shows the results obtained from Bench Top Permeability System. From the results, the percentage of permeability reduction can be calculated.

Table 4.5: Effective Permeability of Core Samples

Aqueous Solution	Effective Permeability (mD)		Percentage of Permeability Reduction (%)
	Initial	Final	
Barium Chloride (treated)	166.68	111.54	33.08
Barium Chloride (untreated)	166.68	94.91	43.06
Sodium Sulfate (treated)	85.30	50.92	40.30
Sodium Sulfate (untreated)	85.30	33.29	60.97

Based on result in Table 4.5, the percentage of permeability reduction of barium chloride solution (treated with the ZSM-5) is smaller compared to the percentage of permeability reduction for the untreated barium chloride solution. The results is also the same the for sodium sulfate solution, where the treated sample solution has lower percentage of permeability reduction compare to untreated sample solution.

The higher percentage of permeability reduction for untreated sample solutions might cause by blocking or precipitation of the inorganic scaling at pore space of the core sample. Thus, this will reduce the permeability of the core samples. In this test, ZSM-5 has shown its ability in mitigating inorganic scaling since there are only small percentages of permeability reduction for the treated sample solution compared to untreated one.

CHAPTER 5

CONCLUSION & RECOMMENDATIONS

5.1 Conclusion

Inorganic scaling is a predominant formation damage mechanism in most producing and injection wells worldwide. The mitigation of inorganic scaling is very important as it can lead to other problems such as plugging of flow channels in the formation and across the perforation, and scaling on downhole tool assembles and surface facilities. Hence, the purpose of this project is to analyze the potential of synthetic zeolite in mitigating inorganic scaling, as it has the high selectivity and high ion exchange capacity.

Based on the results obtain from the XRF analysis and permeability test, the synthetic zeolite, ZSM-5 has shown its ability in mitigating inorganic scaling. In the XRF analysis, the chemical elements of ZSM-5 have been analyzed. There are some traces of sodium and barium that have been adsorbed by ZSM-5. Meanwhile, for the results obtained from the permeability test, ZSM-5 has also shown its potential in mitigating inorganic scaling. It has been proved by some changes in permeability of the core samples based on the sample solution used to saturate the cores. The treated sample solution shows lower percentage in effective permeability reduction compared to the untreated sample solution. Hence, the synthetic zeolite has proved its potential in mitigating inorganic scaling.

5.2 Recommendations

Based on the results obtained from this project, some of the elements need to be improved in order to obtain the better results in future research:

(i) Improving the experimental setup for zeolite ion exchange experiment:

As mention before there are some problems occur during the ion exchange process, since the synthetic zeolite, ZSM-5, is not readily susceptible to ion exchange due to the hindrance from bulky quaternary cations and occluded organic materials which are believed to be located in the channel system. Therefore, in order to obtain intrinsic ion exchange information, these bulky organics must be removed and replaced by smaller cations such as Na^+ or $NH4^+$. Thermal and chemical treatments are effective modes of removal of organic. In addition, the ion exchange isotherms can be obtain from batch experiments conducted in a constant temperature agigated system utilizing tightly sealed polypropylene bottles most if the exchanges are carried out at ambient temperature for 24 to 72 hours.

(ii) Using other equipment or alternative in order to measure the potential of synthetic zeolite in mitigating inorganic scaling:

In order to analyze or examine the potential of synthetic zeolite in mitigating inorganic scaling, other equipments such as Atomic Adsorption Spectrophotometer (AAS) can also being used as to measure the concentration of an identified metal ion in a particular solution. The reduction of sample solution concentration (after treated with synthetic zeolite), will indicates the potential of synthetic zeolite in mitigating inorganic scaling.

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APPENDIX 1: Calculation of Quantity of Barium Chloride

Quantity of barium chloride in the solution containing 1000ppm barium ions

Molecular weight of $BaCl_2.2H_2O$ = 244.28 g/mol

Molecular weight of Ba = 137.33 g/mol

Percentage of Ba in $BaCl_2.2H_2O$ $= \frac{137.33 g/mol}{244.28 g/mol} \times 100\%$

$= 56.22\%$

Concentration of $BaCl_2.2H_2O$ to give 1000 ppm Ba $= \frac{100\%}{56.22\%} \times 1000 mg/L$

$= 1.779$ g/L

Amount of $BaCl_2.2H_2O$ in 1 liter solution = 1.779 g/L x 1 L

= 1.779 g

APPENDIX 2: Calculation of Quantity of Sodium Sulfate

Quantity of sodium sulfate in the solution containing 1000ppm sodium ions

Molecular weight of Na_2SO_4 = 142.04 g/mol

Molecular weight of Na = 22.99 g/mol

Percentage of Na in Na_2SO_4 $= \frac{22.99 g/mol}{142.04 g/mol} \times 100\%$

$= 16.19\%$

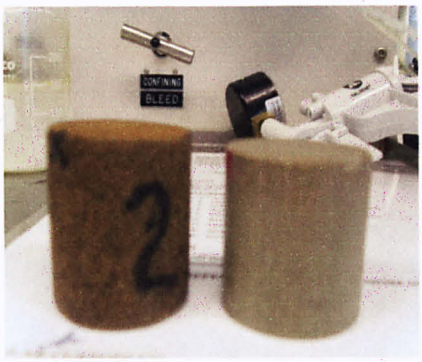
Concentration of Na_2SO_4 to give 1000 ppm Na $= \frac{100\%}{16.19\%} \times 1000 mg/L$

$= 6.177$ g/L

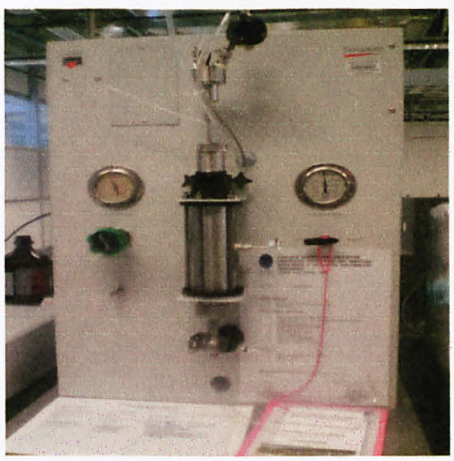
Amount of Na_2SO_4 in 1 liter solution = 6.177 g/L x 1 L

= 6.177 g

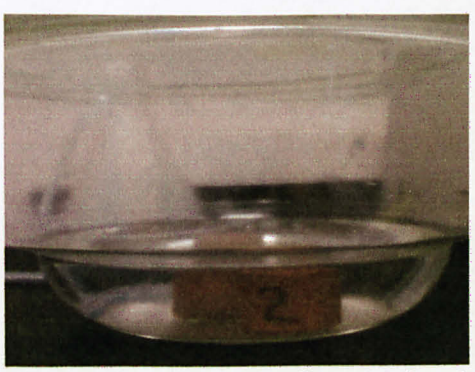
APPENDIX 3: Core Sample Preparation before Permeability Test



Core Samples used for the Permeability Test



PoroPerm System



Saturate the Core Sample with the Sodium Sulfate in Desiccators

APPENDIX 4: Formula and Calculation for Permeability Test

1) Formula to Calculate the Permeability

The value of effective permeability obtained from the Bench Top Permeability system can be calculated by using the Darcy's Law:

i) Permeability, k:

$$k = \frac{14700 \times \mu \times Q \times L}{A \times \Delta P}$$

where

k = permeability, mD

μ = viscosity, cp

Q = flow rate, cc/sec

A = cross sectional area of flow, cm^2

ΔP = pressure difference across the length, L

L = length of sample, cm

ii) Cross sectional area of flow, A:

$$A = \frac{\pi D^2}{4}$$

where

D = diameter of the core sample, cm

2) Calculation of Percentage of Permeability Reduction (%)

$$= \frac{\text{Initial permeability} - \text{Final Permeability}}{\text{Initial Permeability}}$$

$$= \frac{1666.8 - 111.54}{1666} \times 100$$

$$= 33.8\%$$